Dynamics of Elementary Termolecular Reactions and Cluster Fragmentation

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1. Objectives

The objectives of this research project were to characterize the dynamics of neutral three-body dissociation reactions important in the atmosphere and to study the structure and dynamics of potential energetic materials of interest to the US Air Force. In brief, a new type of photoelectron-photofragment spectrometer was constructed with the assistance of both the AFOSR and the David and Lucile Packard Foundation, employing a unique multiple photofragment detector to allow the characterization of three-body dissociation processes. With this apparatus, negative-ion photodetachment was used to prepare transient neutral molecules and clusters as precursors to three-body dissociation reactions. The work focused on environmentally relevant ozone-water complexes and potential energetic materials, such as oxygen and nitrogen-oxygen clusters. The notable results include insights into the structure of the $O_3^-(D_2O)$ complex and the O_6^- complex, the observation that the triplet excited states of O_3 are not quenched by complexation with D_2O, and the characterization of isomeric forms of $N_3O_2^-$ and $N_2O_2^-$.

2. Accomplishments/ Findings 6/1/96 - 11/30/99

2a. Apparatus

A central element of this research project was the development of a new type of fast-ion beam spectrometer. The photoelectron-multiple photofragment spectrometer is a second-generation apparatus, and allows some of the first coincidence measurements of both synchronous and asynchronous three-body dissociation processes in neutral molecules to be carried out. The ion source of the apparatus is similar to that previously used in our laboratory, and makes use of electron impact on a pulsed free jet expansion, followed by acceleration and mass-selection by time-of-flight. The apparatus features two opposed photoelectron detectors, orthogonal to the ion beam axis, which more than doubles the photoelectron detection efficiency compared to the first apparatus. The most unique aspect of the apparatus, though, is the multi-particle detector. This detector makes use of microchannel-plate particle amplification followed by time- and position-sensitive detection using a novel crossed-delay-line anode. The crossed-delay-line technology has been previously developed and applied to extreme ultraviolet astronomy using satellite-based detectors at the UC Berkeley Space Sciences Laboratory. Application of this technology to chemical dynamics has been carried out in our laboratory for the first time.

The new detector anode is called the quadrant-crossed-delay-line (QXDL) anode because it is composed of four identical quadrants. The anode was constructed using multi-layer high-speed electronic circuit board fabrication techniques. The electrons produced by the microchannel plates first encounter a series of conducting strips which are connected to, say, the x-coordinate delay line. Depending on the position-of-arrival, the pulse recorded at each end of the delay line will vary linearly. Measurement of this time difference allows the position to be determined. These strips are separated from the lower strips by appropriate dielectric materials and insulating ground planes. Laser ablation techniques are used in the fabrication to expose the lower set of strips which are connected to the y-coordinate delay line. From a given pulse of electrons, approximately half are collected on each delay line, allowing the determination of the x,y and t coordinates for the particle striking the microchannel plate. Using high-resolution timing techniques, the delay line signals can be measured with ≈50 ps resolution, yielding position uncertainties of ≈100 μm. An important advantage of using fast timing pulses to determine the positions is that these fast pulses can be rapidly processed. Using custom-built electronics thus allows for the detection of more than one particle per anode given an inter-particle separation of more than 25 ns. This feature should allow the QXDL to record three-body dissociation events in coincidence for nearly all kinematics and angular distributions. This detector is the only one of its kind, and is now beginning to produce results as discussed below.

An important component of this apparatus is a Ti:Sapphire laser which produces transform-limited 1 ps pulses at 775 nm. This laser was obtained through the AFOSR DURIP program, and with support from UCSD. The experiments with this laser to date have used the fundamental, 2nd and 3rd harmonics of this laser. We hope in the future to use this laser to generate vacuum ultraviolet radiation to study higher lying excited states of molecules potentially relevant to high temperature reacting flows, such as $O(H_2O)$ complexes.

2b. Three-Body Dissociative Photodetachment of $O_3^-(D_2O)$

The three-body recombination reaction $O + O_2 + M \rightarrow O_3 + M$ is responsible for the formation of stable ground state O_3 in the atmosphere. Therefore this system is an important prototypical three-body system for our detailed dynamics studies.

The study of this system first focused on photoelectron spectroscopy to provide information on the energetics of the system. From these studies, we determined that $O_3^-(D_2O)$ is bound by 0.75 eV relative to $O_3^- + D_2O$, and that the electronic structure of O_3^- is largely unperturbed by clustering with D_2O via a charge-dipole interaction. Since three-body dissociative photodetachment can only be observed by photodetachment to one of the low-lying dissociative electronic states of O_3, this meant that an ultraviolet laser had to be used. In the present study, we used the 258 nm 3rd harmonic of a Ti:Sapphire laser. With these 4.80 eV photons, the dissociative states of the complex could be prepared. The interesting three-body intracluster reaction, $O_3(D_2O) \rightarrow OD + OD + D_2O$, however, is only energetically accessible by 0.16 eV. Since dissociation of the lowest triplet and singlet excited states populated by photodetachment at 258 nm yield ground state $O(^3P)$ which is expected to have a large barrier for hydrogen abstraction from water, it was not surprising that we observed no evidence for this reaction pathway.

In paper 6 of section 4.a, we reported the photoelectron-photofragment kinetic energy correlation spectrum for $O_3^-(D_2O)$ at 258 nm. This spectrum illustrates the correlation between the translational energy release (E_T) between the fragments and the photoelectron kinetic energy (eKE). The E_T spectrum for $O_3^-(D_2O)$ features a broad peak with a maximum at 0.45 eV. This is very similar to the dissociative photodetachment of free O_3^-, previously studied in this laboratory. The eKE spectrum has considerably less resolved structure than that of free O_3^-, which is perhaps not surprising given the larger number of degrees of freedom and the potentially much faster predissociation in the perturbed complex. The similiarties with free O_3^-, however, indicate that energy partitioning in the three-body dissociative photodetachment of $O_3^-(D_2O) + h\nu \rightarrow O + O_2 + D_2O + e^-$ is little affected by the presence of the third body, D_2O.

The detailed dynamics of the three-body dissociation of the excited $O_3(D_2O)$ complex can be studied by examining the angular correlations of the product recoil vectors. Since all the products are detected in coincidence, this can be done in the present experiments and presented in the form of a new observable, the molecular frame-differential cross section (MF-DCS). The MF-DCS is generated by transforming the data from the laboratory frame to a molecular break-up frame such that for each event, the velocity vector of the O atom is chosen as the principal axis and the recoil velocities of the other two particles are then plotted in this center-of-mass reference frame as shown in Figure 2. The mass-resolution in these experiments is currently limited -- O_2 can be fully resolved from O and D_2O, but they cannot be fully resolved from one another. Due to this limitation, the assumption is made in generation of the MF-DCS that the O atom is the fastest particle. The MF-DCS shows that the centroid of the O_2 distribution recoils backward relative to the O atom, while the centroid of the D_2O feature is actually observed to be slightly forward-scattered relative to the recoiling O atom. The striking result from the MF-DCS is that the product momenta are partitioned such that the heaviest fragment, O_2, carries away most of the momentum, with the lighter O and D_2O fragments recoiling in the other direction in the CM.

To gain further insights into the three-body dissociation dynamics indicated by the MF-DCS, we have carried out density functional theory (DFT) calculations of the structure of the parent $O_3^-(D_2O)$ complex. Two local minima were found, an asymmetric C_s complex with D_2O hydrogen bonded to one end of O_3^- and a double-hydrogen-bonded C_{2v} complex. By using the MF-DCS in conjunction with these DFT calculations, the most likely geometry of the complex at the time of the molecular break-up was deduced. In the structure with C_s symmetry, the cluster only forms one hydrogen-oxygen interaction between the two monomers. The calculated C_s geometry indicates that the O-D bond in the water moiety and the O-O_2 bond nearest the intracluster interaction are both longer than their respective ground state bond lengths, consistent with an ion-dipole interaction between the two moieties. This breaking of the C_{2v} symmetry of O_3 in the cluster is expected to promote the antisymmetric stretch dissociation of the lengthened O-O_2 bond, which has been shown to be the reaction coordinate for dissociation of the low-lying excited states of O_3 in previous studies. This initial structure can be consistent with the observed partitioning of momentum if the lengthened bond breaks, causing the recoiling O atom to interact nearly elastically with D_2O, but in the process transferring a significant fraction of its momentum to the D_2O. The heavier O_2 product then carries away most of the momentum as it recoils in the other direction. Dissociation of the C_{2v} symmetry complex would not be expected to lead to such a striking partitioning of momentum between the light and heavy fragments.

To summarize, these experiments on the DPD of $O_3^-(D_2O)$ provided insights into the energetics of the anion and the three-body dissociation dynamics of excited electronic states of the neutral complex. Photodetachment to the triplet states of O_3 in the complex leads to three-body dissociation, with no clear evidence observed for intracluster reaction or quenching of the excited states in the complex at the level of excitation used in this experiment. In addition, the MF-DCS shows that the partitioning of momentum among the products leads to most of the momentum carried away by O_2, with O and D_2O recoiling in the opposite direction in the CM. Combining the observations made from the MF-DCS and theoretical calculations, it is possible to make structural inferences on the dissociating neutral complex and the precursor anion. The results are most consistent with an $O_3^-(D_2O)$ complex of C_s symmetry found by DFT calculations. In ongoing experiments, we are going to examine potential isotope effects in the three-body dissociation dynamics of ozone-water clusters (with one, two or more clustered waters) using ^{18}O labeled complexes. An important feature of these studies is that we will apply an electrostatic focusing technique prior to photodetachment which is expected to significantly improve the mass resolution of the experiment by reducing the uncertainty in the beam centroid distribution.

2.c. Three-Body Dissociation Dynamics of O_6^-

Since oxygen plays a central role in both ion and neutral chemistry in atmospheric, plasma and combustion environments, we have continued to study the chemistry of clusters of oxygen. Building on our earlier studies of the dimer anion O_4^-, we have now carried out experiments with the new photoelectron-multiple-photofragment spectrometer that allow a detailed insight into the three-body dissociation dynamics that ensues upon the dissociative photodetachment of O_6^-: $O_6^- + h\nu \rightarrow O_2 + O_2 + O_2 + e^-$. In this system, the photoelectron-photofragment correlation spectrum reveals several processes, and provides considerable insight into the dissociation dynamics of O_6. Four diagonal features are observed in the spectrum, similar to our previous studies of O_4^-, that correspond to direct three-body dissociative photodetachment of $O_6^- + h\nu \rightarrow O_2 + O_2 + O_2 + e^-$ on vibrationally adiabatic repulsive surfaces. The spacing of these features in internal energy corresponds to 0.19 eV, the vibrational spacing of O_2. There are also two other features observed, one arising from the photodissociation $O_6^-+h\nu \rightarrow O_2(^1\Delta_g,v=0)+O_2^-(^2\Pi_g,v=0)+O_2(^3\Sigma_g^-)$. The analogous process was seen in O_4^-. A new process was observed in O_6^-: photodissociation to vibrationally excited O_2^- and the ground states of the two other O_2 products: $O_6^-+h\nu \rightarrow O_2^-(^2\Pi_g,v>3)+O_2(^3\Sigma_g^-)+O_2(^3\Sigma_g^-)$. This process leads to resolved features in the photoelectron spectrum owing to rapid vibrational autodetachment of the $O_2^-(^2\Pi_g,v>3)$ products of this photodissociation. Thus, the addition of a third O_2 to O_4^- has a significant effect on photodissociation processes, but evidently much less influence on the photodetachment dynamics. This is not to say that there is no effect on the O_2 product state distribution, however. The dissociative photodetachment of O_6^- is observed to yield considerably higher vibrational excitation than in the case of O_4^-. This implies that the nuclear and electronic structure of O_6^- is more complicated than simply an O_4^- core with a weakly bound O_2, or alternatively a molecular anion in which the excess electron is fully delocalized over the three O_2 molecules.

2.d. Isomeric Forms of $N_3O_2^-$

An important advantage of coincident photoelectron and photofragment spectroscopies is that these techniques provide complementary information about the stabilization of an anion relative to the neutral (photoelectron spectroscopy) and the repulsive energy present in a neutral formed in a dissociative state relative to the photofragments (photofragment spectroscopy). We have made use of this to study the isomeric forms of $N_3O_2^-$ formed by electron impact on a free jet of N_2O. This study touches on an issue of interest to the Air Force concerning chemistry in the space environment. It is important to know if metastable species produced in supersonic expansions may lead to characteristic optical and thermal emissions in the plumes produced by propulsion systems, providing unique signatures.

$N_3O_2^-$ is of interest because results which are indicative of the existence of multiple isomeric structures, ranging from an ion-dipole complex $NO^-(N_2O)$ to a more stable covalently bound $N_3O_2^-$ molecule, have previously been observed by other researchers. It is of interest in such cases to determine the chemistry of transient isomeric structures under a variety of conditions. Such isomeric structures may play poorly understood roles in exotic environments such as jet and rocket exhaust plumes. This system has been studied previously, with contrasting results, as discussed below. Thus, it appeared to be an ideal case in which to look for isomeric forms of the anion.

The ion-dipole complex $NO^-(N_2O)$ was studied using photoelectron spectroscopy at 514 nm by Bowen and co-workers.[1] Their results showed a long vibrational progression in the NO product, shifted to a higher electron affinity by 0.20 eV. This shift was interpreted as arising from the energy of solvation when N_2O is clustered to NO^-. Hiraoka, on the other hand, has seen evidence for a more stable isomer.[2] Quantitative experimental numbers for this added stability are not available, but *ab initio* calculations by Hiraoka indicated that this covalently bound O-N-N-N-O$^-$ molecule is stabilized by $\approx$1.25 eV. These earlier experiments differ from each other in that Bowen's anions are produced in a cold supersonic expansion, whereas Hiraoka's studies involve thermalized anions in a high-pressure mass spectrometry experiment. Since our existing apparatus has the capability of performing simultaneous measurements of both photoelectron spectra and photofragment translational spectra, we felt that further insights on the dynamics of this molecule could be gained by new measurements.

The $N_3O_2^-$ anion was produced in our laboratory in a supersonic expansion of pure N_2O crossed by a 1 keV electron beam. Anions are produced in the continuum flow region by a variety of electron-impact and secondary electron attachment processes. The anions are cooled in the expansion, and mass-selected by time-of-flight. In this manner, various metastable isomeric species can be 'frozen-out' and studied in the ion beam. The experiments showed a remarkable wavelength dependence of the photoelectron spectra at 532, 355 and 262 nm. At 532 and 355 nm, the spectra were consistent with the solvated NO^- interpretation given by Bowen and co-workers for their earlier photoelectron studies. Evidence for the existence of multiple isomers is observed in the 266 nm spectra. In addition to the characteristic $NO^-(N_2O)$ signal at high electron kinetic energies there are two new features -- a sharp peak at 3.2 eV and a large broad peak at $\approx$0.9 eV. The sharp peak at 3.2 eV is easily identified as arising from photodetachment of O^-, while the new band at $\approx$0.9 eV is unassigned at this point.

Since production of O^- from the photodissociation of NO^- is not observed to occur, the observation of O^- photodetachment indicates occurrence of a new ion photodissociation channel. Consideration of possible known products of this photodissociation indicates that the most likely candidate for this channel is the reaction $N_3O_2^- + h\nu \rightarrow N_2 + NO + O^-$. The occurrence of this three-body dissociation is further indicated by the fact that no two-body ion photodissociation channel was identified. In addition, the N_3O molecule is not known to exist. A possible explanation of this pathway involves photo-assisted dissociative attachment on N_2O.[3] The

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1. J.V. Coe, J.T. Snodgrass, C.B. Freidhoff, K.M. McHugh, and K.H. Bowen, J. Chem. Phys. **87**, 4302 (1987).
2. K. Hiraoka, S. Fujimaki, K. Aruga, and S. Yamabe, J. Phys. Chem. **98**, 8295 (1994).
3. J.M. Parnis, L.E. Hoover, D.B. Pedersen, and D.D. Patterson, J. Phys. Chem. **99**, 13528 (1995).

electron photodetached from NO may collide with the nearby N_2O molecule, leading to the well-known dissociative attachment reaction $N_2O + e^- \rightarrow NO + O^-$. It is unclear why this channel would only be observed at 266 nm, however, as the cross-section for this process is known to peak at an electron energy of 2.5 eV.[4] Photodetached electrons at an energy of ≈2.5 eV would be most efficiently produced at 532 nm.

An important feature of our apparatus is, however, that we can also record the photofragment translational energy release spectra. Consider photodetachment of the ion-dipole $NO^-(N_2O)$ complex. Given the small degree of solvation noted in this weakly bound cluster anion, it will be expected that there is little repulsive energy in the nascent neutrals. Thus, the energy released in translation between the NO + N_2O photofragments is expected to be small. This is in fact observed to be a major channel as shown in the product translational energy distributions. Large peaks below 0.1 eV in the data represent the vast majority of the photofragments. At all wavelengths, a higher translational energy release channel is also observed. This channel peaks at 0.8 eV at 532 nm, increasing slightly in energy with decreasing wavelength to 1.0 eV at 266 nm. This indicates that some fraction of the NO + N_2O molecules are produced with significant repulsive energy.

The correlation of the photoelectron kinetic energy with the photofragment translational energy release at 266 nm confirms that the broad signal seen at low photoelectron kinetic energies is correlated with the high kinetic energy release process. This proves that *photodetachment* of $N_3O_2^-$ accesses a region of the NO + N_2O neutral surface which is characterized by a significant repulsion and hence a large translational energy release.

To summarize, then, our results have confirmed that there are at least two forms of $N_3O_2^-$ produced in our ion source: the ion-dipole complex and a more stable covalently bound species as proposed by Hiraoka. Dissociative photodetachment of the ion-dipole complex is observed to lead to small translational energy release. Dissociative photodetachment of the covalently bound complex, however, leads to a large kinetic energy release between NO + N_2O. And, most importantly, evidence is observed for a three-body dissociation process, most likely producing O^- + N_2 + NO.

2.e. Excited State Dynamics of N_2O_2 and the Dissociative Photodetachment of $N_2O_2^-$

Our study of the excited state dynamics of N_2O_2 by the dissociative photodetachment of $N_2O_2^-$ once again illustrates the power of photoelectron-photofragment coincidence spectroscopy to elucidate the role played by isomeric forms of molecular anions. Work from Mark Johnson's laboratory initially showed that several isomers of $N_2O_2^-$ could be prepared: an weakly bound complex $O_2^-(N_2)$, a covalent species thought to be the C_{2v} NNO_2^- isomer, and the $(NO)_2^-$ dimer anion. Neumark's laboratory later carried out photoelectron spectroscopy and photodissociation experiments on the species thought to be the NNO_2^- isomer. These experiments showed for the first time resolved vibrational structure in the photoelectron spectra, indicating that bound excited states of N_2O_2 could be accessed by photodetachment. This was an exciting result, since

[4]. P.J. Chantry, J. Chem. Phys. **51**, 3369 (1969).

calculations by Mark Gordon's group and others had indicated that some of the excited states of N_2O_2 have potential application as energetic materials. It was in this context that we carried out our experiments on what was nominally this C_{2v} NNO_2^- isomer, formed by electron impact on a neat expansion of N_2O.

The photoelectron spectra we recorded at 266 nm, while at a somewhat lower resolution, reproduced the structure earlier observed by Arnold and Neumark. Since our apparatus can record the photofragment mass and kinetic energy distributions in coincidence with the photoelectrons, however, we immediately learned that the excited states of N_2O_2 produced by photodetachment dissociate via two pathways: $N_2O_2 \rightarrow NO + NO$ and $N_2O_2 \rightarrow O + N_2O$. Furthermore, since we measure the total translational energy released, including the photoelectron and the photofragments, the stability of the parent anion can be directly determined. Conservation of energy in the total translational energy spectra demands two isomeric forms of the $N_2O_2^-$ parent, with stabilities differing by $\approx$ 0.6 eV. We also infer, in accord with recent theoretical calculations by Snis and Panas, that the more stable isomer $(NO)_2^-$ dissociates to $NO + NO + e^-$, while the C_{2v} NNO_2^- isomer dissociates to $O+N_2O+e^-$. No evidence for excited states of N_2O_2 stable on the $\approx$10 μs flight time were observed in these experiments. This is the first direct measure of the stability (or lack thereof) of the excited states of N_2O_2, and once again demonstrates the power of the photoelectron-photofragment coincidence technique to prepare and study transient neutral species of interest as energetic materials.

2.f. Work in Progress: Three Body Dissociative Photodetachment of $O^-(H_2O)_2$ and $OH^-(H_2O)_2$ and Deuterated Analogues

Current experiments focusing on the interaction of reactive species such as the O atom and the OH radical with solvating water molecules are underway. The three-body dynamics in these systems may yield insights into the behavior of these reactive species in both condensed and high-pressure gas-phase environments, such as might be encountered in an expanding rocket exhaust. In the case of $O^-(D_2O)_2$, we have acquired the photoelectron-photofragment correlation spectrum and the MF-DCS. In this system two product channels are accessible, $O + 2\ D_2O + e^-$ and $OD + OD + D_2O$. Regrettably the current mass-resolution of the experiment prevents a clean resolution of these channels, although a significant difference in the energetics allows the former channel to be studied in isolation for low levels of product excitation. The MF-DCS in this system shows that all three products carry away comparable amounts of linear momentum, in striking contrast to the previously studied systems, O_6^- and $O_3^-(D_2O)$. In the case of O_6^-, two of the O_2 products carry away equal momenta, imparting only a small amount to the third O_2. In the case of $O_3^-(D_2O)$, the heavy product, O_2, carries away most of the momentum. Calculations of the structure of the $O^-(D_2O)_2$ anion are underway to aid in the interpretation of these observations. We have now also shown that the $OH^-(H_2O)_2$ system can be prepared in good quantities, and have already observed three-body dissociative photodetachment in this system. In this system, only one product channel, $OH + 2\ H_2O + e^-$, is accessible so mass resolution is not a critical issue.

3. Personnel Associated with the Research Effort

1. A number of personnel have received full or partial support from this grant:

Graduate Students: Todd Clements, Mark Garner, Leah Alconcel

Undergraduate Students: Jacqueline Kessler, Raymond Liu

2. Other personnel have worked on these projects with outside support:

Graduate Students: A. Khai Luong (AASERT), Jacqueline Kessler (AASERT), Raymond Liu (AASERT)

Postdoctoral Fellows: Karl Hanold, Runjun Li, Marianne Resat, Veysel Zenging (David and Lucile Packard Foundation)

4. Publications

In the period of this grant, six peer-reviewed papers appeared. An additional three are in press and one is still in preparation. These contributions are enumerated here.

4.a. Published

1. R.Li, K.A. Hanold, M.C. Garner, A.K. Luong and R.E. Continetti, "Excited State Dynamics in Clusters of Oxygen.", Discussions of the Faraday Society, **No. 108**, 115-130 (1998).

2. M.S. Resat, V. Zengin, M.C. Garner and R.E. Continetti, "Dissociative Photodetachment Dynamics of Isomeric Forms of $N_3O_2^-$.", J. Phys. Chem. **102**, 1719-1724 (1998).

3. R.E. Continetti, "Photoelectron-Photofragment Coincidence Studies of Dissociation Dynamics.", Int. Rev. Phys. Chem. **17**, 227-260 (1998).

4. K.A. Hanold, A.K. Luong and R.E. Continetti, "Complete Kinematic Measurement of Three-Body Reaction Dynamics: Dissociative Photodetachment of O_6^- at 532 nm.", Journal of Chemical Physics, **109**, 9215-9218 (1998).

5. K.A. Hanold, A.K. Luong, T. Clements and R.E. Continetti, "Photoelectron-Multiple-Photofragment-Coincidence Spectrometer.", Review of Scientific Instruments **70**, 2268-2276 (1999).

6. A.K. Luong, T.G. Clements and R.E. Continetti, "Three-body Dissociation Dynamics of Excited States of $O_3(D_2O)$.", J. Phys. Chem. **103**, 10237-10243 (1999).

4.b. In Press

1. R.E. Continetti, "Dissociative Photodetachment Studies of Transient Molecules by Coincidence Techniques.", to appear in Advanced Series in Physical Chemistry: Photoionization and Photodetachment, ed. C.Y. Ng, World Scientific, Singapore (2000).

2. A.K. Luong, T.G. Clements and R.E. Continetti, "Three-body Dissociation Dynamics of Neutral Transient Species: Dissociative Photodetachment of O_6^-.", ACS Symposium Series on Imaging in Chemical Dynamics, eds. A.G. Suits and R.E. Continetti, submitted Dec. 1999.

3. A.G. Suits and R.E. Continetti, "Imaging in Chemical Dynamics: The State of the Art.", ACS Symposium Series on Imaging in Chemical Dynamics, eds. A.G. Suits and R.E. Continetti, submitted Dec. 1999.

4.c. In Preparation (to be submitted in 2000)

1. R. Li and R.E. Continetti, "Studies of the Excited State Dynamics of N_2O_2 by Dissociative Photodetachment of $N_2O_2^-$.", to be submitted to J. Chem. Phys. (2000).

5. Interactions/Transitions

5.a. Meetings

The P.I. has given 26 invited talks at a number of institutions, including both academic and government research laboratories. This has included two talks at Hanscom AFB and one at Edwards AFB. The P.I. has also been an invited speaker at a number of national and international meetings in this time frame. AFOSR-sponsored work was reported on at the following meetings. Note that the invited talk at the ACS National Meeting in New Orleans in 1999 was given by the PI's student A. Khai Luong, an AASERT fellow.

1. "Dissociative Photodetachment Studies of Transient Molecules.", 24th International Symposium on Free Radicals, Taellberg, Dalecarlia, Sweden, Aug. 20, 1997.
2. "Dissociative Photodetachment Probes of Isomeric Forms of Molecular Anions.", 214th ACS National Meeting, Las Vegas, NV, Sept. 10, 1997.
3. "Excited State Dynamics in Clusters of Oxygen", Faraday Discussion 108 on Dynamics of Electronically Excited States in Gaseous, Cluster and Condensed Media, University of Sussex, UK, December 16, 1997.
4. "Dissociative Photodetachment Studies of Molecular Negative Ions", Symposium on Structure and Dynamics of Atomic and Molecular Negative Ions, University of Aarhus, Aarhus, Denmark, May 19, 1998.
5. "Photoelectron-Photofragment Coincidence Studies of Dissociation Dynamics", Gordon Research Conference on Multiphoton Processes, Tilton School, Tilton, New Hampshire, June 16, 1998.

6. "Photoelectron-Photofragment Coincidence Studies of Two- and Three-Body Dissociation Dynamics."Gordon Research Conference on Atomic and Molecular Interactions, Colby Sawyer College, New London, New Hampshire, July 1, 1998.
7. "Dissociative Photodetachment Probes of Three-Body Collisions.", Gordon Research Conference on Photoions, Photoionization and Photodetachment, Plymouth State College, New Hampshire, July 18-23, 1999.
8. "Dissociative Photodetachment Studies of Transient Molecules.", 19th International Conference on Photochemistry, Duke University, Durham, North Carolina, August 1-6, 1999.
9. "Three-body dissociation dynamics of the ozone-water complex.", Symposium on Imaging in Chemical Dynamics, 218th ACS National Meeting, New Orleans, August 22-26, 1999, (presented by student A. K. Luong).

In addition to these presentation at meetings, the PI was also a co-organizer of three symposia during the period of this grant:

Co-organizer, SPIE conference, "Laser Techniques for State-Selected and State-to-State Chemistry IV", January 29-31, 1998, with John Hepburn and Mark A. Johnson.

Co-organizer, ACS Symposium, "Imaging in Chemical Dynamics", 218th ACS National Meeting, New Orleans, August 24-26, 1999, with Arthur G. Suits.

Co-organizer, Pacifichem 2000 Symposium, "New Frontiers in Chemical Reaction Dynamics", Honolulu, Hawaii, December 14-19, 2000.

The PI was also invited to attend the following two meetings by the National Academy of Sciences and the National Research Council, respectively.

Participant, 2nd Annual Chinese-American Frontiers of Science Symposium, Chinese Academy of Sciences/US National Academy of Sciences, Beijing, China, August 20-22, 1999.

Participant, NRC Chemical Sciences Roundtable Meeting on the Future of Graduate Education, Washington, DC, December 5-6, 1999.

5.b. Consultative/Advisory Functions

Over the period of this grant, the PI interacted on numerous occasions with AFRL researchers:

1. Consultations via e-mail with Drs. Steven Singleton and Steven Miller of the Phillips Lab, Hanscom AFB (PL/GPOS) concerning the photodissociation cross-section of N_3 in 1996. Based on earlier work done by the P.I., an estimate of $\sigma > 10^{-20}$ cm^2 was provided to Dr. Singleton, who was looking for controlled sources of N(^{4}S) and N(^{2}D) atoms for studies of the reaction $N+O_2$. Communication with Dr. Steven Miller during a visit to the Phillips Lab on August 27-28 1996 indicated that this work was not successful, however.

2. The P.I. consulted with Dr. Rainer Dressler at the Phillips Lab, Hanscom AFB (PL/GPOS) concerning isomeric structures of cluster anions in 1997.

3. The P.I. hosted visits to UC San Diego by AFRL researchers Dr. Skip Williams in 1998 and Dr. Al Viggiano in 1999. When Dr. Viggiano visited UCSD, we discussed the possibilities of studying dissociative recombination reactions pertinent to high temperature combustion of jet fuels in hypersonic aircraft. No concrete plans have emerged from this discussion yet, due to the expense of modifying our apparatus for such studies.

4. The P.I. has also been in contact with Dr. Ingrid Wysong at AFRL Edwards. This included a visit to AFRL Edwards in October 1999. These discussions have focused on the potential to determine product state distributions in reactions of O atoms and water molecules. We are currently carrying out studies of O + H_2O for DOE, but to make a connection to high pressure phenomena, we are studying the $O(D_2O)_2$ system as discussed in the results section above. In September 1999, the P.I. will visit this group at AFRL Edwards.

5.c. Transitions

The P.I. has developed a collaboration with Dr. Carl Hayden at the Combustion Research Facility at Sandia National Laboratories, Livermore that has continued since the fall of 1997. This collaboration has resulted in the construction of the photoionization version of the photoelectron-photofragment spectrometers pioneered in the P.I.'s laboratory. The first published paper from this work has now appeared. These results are continuing with efforts to implement delay-line detector technology, as pioneered in the quad-crossed-delay-line detector used in the studies of three-body dissociation processes reported here.

6. New Discoveries, Inventions or Patent Disclosures

Outside of the results reported in the accomplishments/new findings section above, there is nothing further to report here.

7. Honors/Awards

In the period of this grant, the P.I. received a Camille Dreyfus-Teacher Scholar Award in 1996. The P.I. also received an Alfred P. Sloan Research Fellowship in 1997. These fellowships were given in recognition of the research accomplishments and future potential of the P.I.

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13. ABSTRACT *(Maximum 200 words)*
A central element of this research project was the development of a new type of fast-ion beam spectrometer. The photoelectron-multiple photofragment spectrometer is a second-generation apparatus, and allows some of the first coincidence measurements of both synchronous and asynchronous three-body dissociation process in neutral moleculeas to be carried out. The ion source of the apparatus is similar to that previously used in our laboratory, and makes use of electron impact on a pulsed free jet expansion, followed by acceleration and mass-selection by time-of-flight. The apparatus features two opposed photoelectron detectors, orthogonal to the ion beam axis, which more than doubles the photoelectron detection efficiency compared to the first apparatus. The most unique aspect of the apparatus, though, is the multi-partical detector. This detector makes use of microchannel-plate particle amplification followed by time- and position-sensitive detection using a novel crossed-delay-line anode. The crossed-delay-line technology has been previously developed and applied to extreme ultraviolet astronomy using satellite-based detectors at the UC Berkely Space Sciences Laboratory. Application of this technology to chemical dynamics has been carried out in our laboratory for the first time.

14. SUBJECT TERMS
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